Ferromagnetism and Spin Waves in the Band Theory

DANIEL C. MATTIS
Thomas J. Watson Research Center, International Business Machines Corporation, Yorktown Heights, New York

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Intra-atomic exchange (Hund's rule mechanism) and Heisenberg nearest-neighbor exchange are examined for their role in the ferromagnetism of metals with degenerate bands. We examine the ground state, and find there is ferromagnetism once the largest eigenvalue j_{00} of the exchange matrix exceeds $\frac{1}{2}\times$No. of atoms/density of states at the Fermi surface. We then find several spin-wave spectra, of which one "acoustic" and at least one "optical" spectrum have infinite lifetime in the random phase approximation. The initial parabolic behavior of the acoustic spectrum yields Bloch's $T^{3/2}$ low at low temperature. There is a maximum wave vector beyond which no spin-wave solutions exist, corresponding to a minimum wavelength of at least several atomic distances. Formulas are given, and the copious numerical results calculated by W. Doherty on the IBM-7094 computer are summarized in graphs and tables. The ferromagnetic ground state is stable versus antiferromagnetic states only so long as umklapp is neglected. Because umklapp is most important in half-filled bands, we find qualitative agreement with previous calculations that antiferromagnetism can result in this case.

INTRODUCTION

WHEN electrons form bands, their magnetic properties must be explained by band theory. The object is to isolate the magnetic behavior from the continuum of electronic states. How much easier is the problem in insulating magnetic materials, in which the energy gap against electronic excitations allows the low-lying magnetic spectrum to be well-separated from the excited electronic states.

And what of the mechanism? Everyone will agree that the Coulomb interaction, and/or "exchange," are at the bottom of the phenomena of magnetism. But what is "exchange"? There is almost no other force which is so representation-dependent, so vague and tenuous, and yet has such important consequences. We shall use the Wannier representation to define it, unambiguously (if perhaps not uniquely). We shall determine when it is strong enough to cause ferromagnetism as a function of the density of states at the Fermi surface. At least 2-fold degenerate bands are required. Once ferromagnetism exists, spin waves do too, and we shall calculate their equation of motion. The initial parabolic behavior, $\hbar\omega \propto q^2$, gives the $T^{3/2}$ law of Bloch. We also find optical spin-wave spectra, and give all the solutions graphically and in tabular form.

We shall discuss the relative importance of Heisenberg nearest-neighbor exchange, and of intra-atomic (Hund's rule) exchange.[1] Both are included in the theory, but the Hund's rule mechanism is favored. Antiferromagnetism is briefly discussed.

HAMILTONIAN

We shall examine the role of exchange in the ferromagnetism of metals, particularly the transition metals Ni or Fe. It is convenient to consider the degenerate, partly occupied d bands as a closed system, and to imagine that the electrons in other (s or p) conduction bands, and those in fully occupied valence bands merely screen the ionic charges of the lattice. Corrections to this can always be accounted for in higher order perturbation theory, or by other means. But the advantages of a closed system are enormous; we need merely to diagonalize, as best we know how, the Hamiltonian in the restricted Hilbert space of the Wannier states of these several bands.

For this purpose it is necessary to know how to express the usual "exchange potential," which is a sum of terms such as

$$-J_{i,t;\,j,t'}\mathbf{S}_{it}\cdot\mathbf{S}_{jt'}, \quad (i,t)\neq(j,t'), \tag{1}$$

connecting an electron on an atom at R_i in band t, and one on R_j and in band t', in terms of the operators that create or destroy an electron with spin $s(=\uparrow$ or $\downarrow)$ in the corresponding Wannier states. The operators obey the usual Fermi anticommutation relations:

$$[c^*_{i,t,s},c^*_{j,t',s'}]_+=[c_{i,t,s},c_{j,t',s'}]_+=0$$
$$[c^*_{i,t,s},c_{j,t',s'}]_+=\delta_{i,j}\delta_{t,t'}\delta_{s,s'},$$
$$c^*_{i,t,s}c_{i,t,s}\equiv n_{i,t,s}=n^2_{i,t,s}. \tag{2}$$

The roles of electrons and holes are reversed merely by interchanging the c's and c^*'s in these expressions and in the Hamiltonian. Also, the set of Fermi operators that create and destroy particles in Bloch states consists of the Fourier transforms:

$$c_{k,t,s}=\frac{1}{\sqrt{N}}\sum_i \exp[i\mathbf{k}\cdot\mathbf{R}_i]c_{i,t,s}$$

[1] E. P. Wohlfarth, Rev. Mod. Phys. **25**, 211 (1953), and also J. H. Van Vleck, Rev. Mod. Phys. **25**, 220 (1953) discussed Hund's rule as a cause for ferromagnetism in the transition elements. They attribute the original idea to Slater [J. C. Slater, Phys. Rev. **49**, 537, 931 (1936)]. Today it is the well-known basis of the indirect exchange theory of the magnetic rare earths; [T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956); S. H. Liu, Phys. Rev. **121**, 451 (1960); Ref. 12] it has been discussed in connection with localized magnetic moments in metals [P. W. Anderson, Phys. Rev. **124**, 41 (1961)] and in such other systems as the O_2 molecule [J. C. Slater, Technical Report #6, Solid State and Molecular Theory Group, M.I.T. (unpublished)].

and

$$c^*_{k,t,s}=\frac{1}{\sqrt{N}}\sum_i \exp[-i\mathbf{k}\cdot\mathbf{R}_i]c^*_{i,t,s}. \quad (3)$$

The three components of the spin vectors are given by,

$$S_p{}^z=\tfrac{1}{2}(n_{p\uparrow}-n_{p\downarrow}),\quad S_p{}^+=S_p{}^x+iS_p{}^y=c_{p\uparrow}{}^*c_{p\downarrow}$$
$$S_p{}^-=S_p{}^x-iS_p{}^y=c_{p\downarrow}{}^*c_{p\uparrow}, \quad (4)$$

where $p\equiv(i,t)$. Therefore, the exchange interaction (1) is quartic in the Fermion operators c_{ps} just as any ordinary two-body interaction. We may note several interesting properties which are made particularly clear in second quantization. If any Wannier state (i,t) is either empty or doubly occupied ($\uparrow$ and $\downarrow$), the exchange operator (1) which refers to the state must vanish. Therefore, the interaction has nonvanishing matrix elements only in the subspace in which Wannier states (i,t) and (j,t') are each singly occupied. It measures the energy splitting between the singlet state

$$\uparrow\downarrow-\downarrow\uparrow,\quad \text{energy } W_0 \quad (5)$$

and the triplet states of the electron pair which were originally degenerate with it

$$\uparrow\uparrow,\quad \uparrow\downarrow+\downarrow\uparrow,\quad \downarrow\downarrow,\quad \text{energy } W_1. \quad (6)$$

The shift is in the amount of

$$W_0-W_1=J_{i,t;\,j,t'}=2\int d^3r\int d^3r'$$
$$\times\{\psi_t{}^*(r-R_i)\psi_{t'}{}^*(r'-R_j)\psi_{t'}(r-R_j)$$
$$\times\psi_t(r'-R_i)\}\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}, \quad (7)$$

where $\psi_t(r-R_i)$ is the Wannier function in band t centered about the atom at R_i. Excluded from this analysis is the case of "self-exchange," when both $i=j$ and $t=t'$. The self-exchange term is diagonal in the Wannier representation and there is no possible triplet involved. Like the direct Coulomb interactions to which we shall shortly turn our attention, self-exchange measures the energy difference between states of varying ionization. This is quite different from the effect of lifting the degeneracy among states of the *same* degree of ionization, as in the case of two different Wannier states, discussed *supra*.

Although the vector model Hamiltonian of Eq. (1) may not always be exact, it provides a particularly compact and qualitatively correct operator formalism for Hund's first rule: "the state of maximum multiplicity lies lowest." This rule, together with Hund's second rule concerning the atomic angular momentum, is invariably obeyed in atomic systems and must therefore be considered of some importance in the solid state. But we have not taken any account of Hund's second rule, which should also have a simple operator representation, beyond what results from the magnitudes of the various Coulomb integrals to which we now briefly turn our attention.

The Coulomb interaction

$$\tfrac{1}{2}\sum_{i,j',t,t',s,s'} n_{i,t,s}n_{j,t',s'}\int d^3r\int d^3r'$$
$$\times|\psi_t{}^*(r-R_i)\psi_{t'}(r'-R_j)|^2\frac{e^2}{|r-r'|} \quad (8)$$

commutes with the exchange interactions (1). It may be considered together with other such forms, including one-body potentials, and combined into a single diagonal interaction

$$V(\cdots,n_{p\uparrow}+n_{p\downarrow},\cdots). \quad (9)$$

Exchange, V, and the kinetic energy comprise our model Hamiltonian for the d bands. The kinetic energy is of course a matrix which is diagonalized only in the Bloch representation, whereas in the Wannier representation it is characterized by the "overlap" $K_{ij,t}$ connecting states in band t centered about R_i and R_j. The Bloch energies $\epsilon_{k,t}$ are therefore just the eigenvalues of the K matrix. Explicitly

$$\text{K.E.}=-\sum K_{ij,t}(c^*_{i,t,s}c_{j,t,s}+\text{H.c.})=\sum \epsilon_{k,t}n_{k,t,s},$$

where

$$\epsilon_{k,t}\equiv-\frac{1}{N}\sum_{i,j}K_{i,j,t}[\exp(ik\cdot(R_i-R_j)+\text{c.c.}]. \quad (10)$$

In this work, we shall consider the effects of exchange and of kinetic energy only, for the purposes of a zeroth-order theory of ferromagnetism and spin waves. This of course allows a tremendous simplification, but it is not an essential one. Within the random-phase approximation, it is quite feasible to consider simultaneously: the Coulomb interaction, the interaction of the d electrons with the other conduction bands, the spin-orbit coupling, all together with the exchange and kinetic energies. But it is the latter two which are responsible for the magnetic moment of isolated atoms, and for the metallic state, respectively, and it is therefore these that we study first. We note that (1) and (10) do not commute, so that the problem is by no means trivial. Nevertheless, it is possible to obtain a quite plausible physical picture and a ground state which, in some limiting cases, is rigorously exact.

It is convenient to combine (1) and (10) into a single expression in terms of Bloch operators. The Fourier relations (3) are easily inverted, and one finds

$$H=\sum_{k,t,s}\epsilon_{k,t}c^*_{k,t,s}c_{k,t,s}-\frac{1}{N}\sum_{k,k',q,K,t,t'\neq t}J_{q,tt'}$$
$$\times\{\tfrac{1}{4}(c^*_{k+q,t,\uparrow}c_{k,t,\uparrow}-c^*_{k+q,t,\downarrow}c_{k,t,\downarrow})$$
$$\times(c^*_{k'-q,t',\uparrow}c_{k'+K,t',\uparrow}-c^*_{k'-q,t',\downarrow}c_{k'+K,t',\downarrow})$$
$$+\tfrac{1}{2}(c^*_{k+q,t,\uparrow}c_{k,t,\downarrow}c^*_{k'-q,t',\downarrow}c_{k'+K,t',\uparrow}+\text{H.c.})\}, \quad (11)$$

where

$$J_{q,tt'}=\frac{1}{N}\sum_{i,j}J_{it;\,jt'}\exp[iq\cdot(R_i-R_j)]. \qquad (12)$$

The ground-state and elementary excitations of this system provide enough information to predict the low-temperature behavior. The neglected interactions, and the more general statistical mechanics of this system pose detailed problems for future investigation. Also left for future study: the effects of intraband exchange, $t=t'$, which, for various reasons, are expected to be small.[2]

Nevertheless, it is of some interest to anticipate quantitative results concerning the direct Coulomb interaction by noting that the correlations must be such as to prevent excess electrons or holes from occupying the same sites, and therefore from lining up their spins. The Coulomb correlations must, therefore, be such as to screen the exchange. But there is also an opposite effect. In the direct Coulomb interaction

$$\sum v(q)\rho_q\rho_{-q} \qquad (8a)$$

there are intraband-exchange terms which enhance the interaction (1) and the magnetic alignment. Indeed, in early theories of magnetism this "exchange scattering" was considered to be the cause of magnetism, in the band theory.[3] Thus, the Coulomb interaction, Eqs. (8) or (8a), gives rise to two competing effects, the one tending to decrease the magnitude of J and the other to enhance it. Moreover, we cannot presume that atomic spectra or atomic calculations can yield the magnitudes of the exchange integrals, because the Wannier functions are more spread out than atomic orbitals, so that both Coulomb and exchange integrals are correspondingly reduced. For all these reasons, it is best to consider the magnitude of the exchange as a parameter to be adjusted to experimental data. Furthermore, in the next section, we shall find that a certain function (of the largest eigenvalue of the exchange matrix and of the density of states at the Fermi surface) turns out to be the most compact "coupling constant," one which is probably best obtained from independent experiments rather than from microscopic calculations.

[2] This commits us to degenerate bands. In the case of a single band, all that remains of our Hamiltonian is the kinetic energy and, therefore, in our model ferromagnetism cannot occur in a nondegenerate band, or for free electrons, in agreement with arguments of Slater [J. C. Slater, Technical Report #6, Solid State and Molecular Theory Group, M.I.T. (unpublished)] and of Wigner [E. P. Wigner, Trans. Faraday Soc. **205**, 678 (1938)].

[3] Similar criteria are found in standard texts, such as A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953), 2nd ed., pp. 182 ff. However, the theory given in this book is based on the direct Coulomb interaction, (see Ref. 6) and there are no spin waves. Thus, correlation is not taken into account [E. P. Wigner, Trans. Faraday Soc. **205**, 678 (1938); also, Refs. 2 and 6], and the low-temperature specific heat and magnetization obey the incorrect T^2 law.

EXCHANGE MATRIX

First, examine the diagonal part of the Hamiltonian,

$$H_{\text{Diag.}}=\sum_{k,t,s}\epsilon_{k,t}n_{k,t,s}-\frac{1}{N}\sum_{t,t'\neq t,k,k'}J_{0,tt'}\times\tfrac{1}{4}(n_{k,t,\uparrow}-n_{k,t,\downarrow})(n_{k',t',\uparrow}-n_{k',t',\downarrow}) \qquad (13)$$

in the Bloch representation. The degenerate Fermi sea, equally populated by spins "up" and spins "down" is an eigenstate of $H_{\text{Diag.}}$, but it is not necessarily the ground state. Among the other eigenstates of varying total-spin angular momentum we single out those, for instance, in which δn states near the Fermi surface are emptied of their spin-up electrons, and an equal number of spin-down electrons are placed in previously unoccupied states closest to the Fermi surface. The resultant magnetization

$$M=-2g\mu_B\delta n \qquad (14)$$

costs a kinetic energy in the *minimum* amount of

$$\frac{1}{2}\frac{(\delta n)^2}{N(0)},\quad \text{for}\quad \delta n\ll n, \qquad (15)$$

with a corresponding *maximum* gain in exchange energy of

$$-\frac{1}{N}j_{00}(\delta n)^2, \qquad (16)$$

where j_{00} is the largest eigenvalue of the exchange matrix $\mathbf{J}_0$, the components of which are the matrix elements $J_{0,tt'}$ defined in Eq. (12), and $N(0)$ is the density of states at the Fermi surface. Once

$$j_{00}\quad\text{exceeds}\quad N/2N(0) \qquad (17)$$

ferromagnetism becomes possible. This is a precise, quantitative statement of the usual band-theoretic criterion, which is that ferromagnetism is favored in narrow bands, but it is the same idea.[3]

It is convenient to choose a sort of "renormalized coupling constant" which increases with increasing ferromagnetism, and which vanishes when the criterion (17) is not satisfied. For this purpose we use the energy Δ which it costs to promote one of the excess spin-down electrons to spin up, without changing its wave vector $\mathbf{k}$ or band index t. It is fortunate that such a simple definition exists for the strength parameter which occurs in all the results to follow, one which is directly amenable to experimental measurement.

In general, we denote the eigenvalues of the matrix $\mathbf{J}_q$, the elements of which are $J_{q,tt'}$, by $j_{qr}(r=0,1,2,\cdots)$ with j_{q0} chosen as the largest.

In order to gauge the dependence on q of these eigenvalues, let us compare the dependence of the exchange integral (7) on the distance (R_i-R_j), with that of the Coulomb integral (8). At large distances the Coulomb

integral becomes inversely proportional to the distance. This leads at once to the well-known Fourier transform $1/q^2$, and the consequent necessity of taking long-wavelength correlations of the electrons into account. On the other hand, if we examine the exchange-matrix elements, and recall that Wannier functions are mutually orthogonal, we see immediately that J must decrease at least as rapidly as the inverse square of the distance. But if, then, one uses the additional fact that the Wannier function is defined so as to be the best localized function about its size R_i which it is possible to construct within a single band, he finds that, practically speaking, there is no exchange among electrons which are more than a few atomic distances apart. As a consequence, the Fourier transforms in this case, far from diverging as $q \rightarrow 0$, must approach constant values in this long-wavelength limit.

Exactly how constant, depends on the following considerations. Apparently the biggest integral occurs when all the functions are centered about the same atom, $R_i = R_j$. If atomic orbitals replaced the Wannier functions in Eq. (7), this would be the same integral as is used in discussing Hund's rule (the magnetic moment of isolated atoms and molecules). Next in importance is the Heisenberg nearest-neighbor exchange mechanism given by the integral (7), when R_i and R_j are nearest neighbors on the lattice. If, for example, Hund's rule exchange gave typical matrix elements of magnitude J_{Hu} and the Heisenberg exchange-matrix elements of typical magnitude J_{Hei}, then the Fourier transform—say on the simple cubic lattice—would be

$$J_q = J_{\mathrm{Hu}} + 2J_{\mathrm{Hei}}(\cos q_x a + \cos q_y a + \cos q_z a), \quad (18)$$

where the components q_x, etc., are restricted to the first Brillouin zone:

$$0 \leq |aq_x|, \quad |aq_y|, \quad |aq_z| \leq \pi. \quad (19)$$

But as we shall always be interested in relatively long wavelengths, the first terms in the expansion

$$J_q = (J_{\mathrm{Hu}} + 6J_{\mathrm{Hei}}) - a^2 J_{\mathrm{Hei}} q^2 + \cdots \quad (20)$$

will be sufficient. How important is the q dependence of the matrix elements? This depends principally on the relative magnitude of

$$(J_{\mathrm{Hu}} + 6J_{\mathrm{Hei}}) \quad \text{and} \quad (J_{\mathrm{Hei}}).$$

SPIN WAVES

The theory of spin waves in metals has been studied in the past.[4] Very plausible arguments have been advanced[4] for why spin waves must exist in metallic ferromagnets, at least for long wavelengths, regardless of the interaction mechanism. No one should be surprised that we now proceed to study the equations of motion of the elementary spin-raising operators

$$S^+_{q,k,t} \equiv c^*_{k+q,t,\uparrow} c_{k,t,\downarrow}, \quad \text{or} \quad c^*_{k+q+K,t,\uparrow} c_{k,t,\downarrow}, \quad (21)$$

with a view to discovering which linear combinations of these are raising operators for the Hamiltonian of Eq. (11), within the random-phase approximation.[5] Using this technique, which is standard by now, we find an implicit equation for the new eigenvalues. Everywhere we indicate by K, that if $k+q$ is not in the first Brillouin zone (B.Z.), it is to be brought back by a reciprocal lattice vector K. Otherwise, $K=0$; this is known as "umklapp." We find[6] It is permissible to suppress the band index t in the energies $\epsilon(k)$, as these are degenerate bands.[7] The new eigenvalues $\hbar\omega_j$ interlace the unperturbed eigenvalues $\Delta + \epsilon(k+q+K) - \epsilon(k)$, except for the bound states which are the spin waves. So long as the spin-wave energies lie outside (either above or below) the continuum of unperturbed eigenvalues, the sum in Eq. (22) may be replaced by an integral, with negligible error. When the solutions merge with the continuum, the lifetime of the collective state becomes so short that it may become merely a resonance, or lose its character entirely. Even so, one may continue the bound-state solutions into the continuum by a simple expedient, such as arbitrarily replacing the sum by a principal parts integration, and this is precisely what we shall now do.

$$1 = \frac{j_{qr}}{N} \sum_k \frac{f\downarrow(k) - f\uparrow(k+q+K)}{\Delta + \epsilon(k+q+K) - \epsilon(k) - \hbar\omega_j}. \quad (22)$$

[4] For example, C. Herring and C. Kittel, Phys. Rev. **81**, 869 (1951); and C. Herring, Phys. Rev. **87**, 60 (1952).

[5] The random-phase approximation and the technique of "equations of motion" (summing all ladder or bubble diagrams) are extensively studied in D. Pines', *The Many-Body Problem* (W. A. Benjamin, Inc., New York, 1962). Our method follows closely the paper by K. Sawada, K. A. Brueckner, N. Fukuda, and R. Brout, Phys. Rev. **108**, 507 (1957), which is reprinted therein, and our Eq. (22) bear resemblance to the dispersion equation for the plasmons.

[6] Similar equations have previously been found in this manner by T. Izuyama, Progr. Theoret. Phys. (Kyoto) **23**, 969 (1960), in an unpublished thesis by M. M. Antonoff (Cornell University), or M. M. Antonoff, Bull. Am. Phys. Soc. **8**, 227 (1963) [who also finds a cutoff of $q_{\max}$], in a mimeographed circular in Japanese by K. Yosida and T. Kasuya, by E. D. Thompson, Ann. Phys. N. Y. **22**, 309 (1963), and probably by many others. However, the distinction between the direct Coulomb interaction and the exchange interaction, given in our Eqs. (7) and (8), is not very clear in these earlier theories. As a result, they may predict ferromagnetism in nondegenerate bands as readily as in degenerate bands, in contradiction with the arguments we have discussed (see Ref. 2) and of experimental evidence. Often, one finds Bloch's original band theory of ferromagnetism thus revived in one form or another. Bloch had supposed the direct Coulomb interaction, our Eq. (8), to be the relevant mechanism. This idea was refuted, however, by E. P. Wigner [E. P. Wigner, Trans. Faraday Soc. **205**, 678 (1938)] on sound physical grounds, and the concept of electronic correlations invented by him to show how the Coulomb interaction, even when quite strong, might have little effect on the free-particle nature of the electron gas. Wigner's arguments, however, did not encompass exchange forces such as our Eq. (7).

[7] The cubic crystal field does not lift all the atomic degeneracies, and there are as many as five, or as few as two degenerate d bands which are taken into account in the present theory. Interactions with partly occupied s and p bands are neglected, although not negligible.

If $\epsilon(k)$ is understood to be extended periodically outside the first B.Z., then we may dispense with K entirely. Also, it is convenient to introduce a single Fermi function

$$f(\epsilon_k)\equiv f\downarrow(\epsilon_k),\quad f(\epsilon_k+\Delta)=f\uparrow(\epsilon_k). \tag{23}$$

Then, after some elementary simplification, the integral equation becomes

$$\text{P.P.}\int d^3k\{f(\epsilon_k)-f(\epsilon_{k+q}+\Delta)\}\times\left\{\frac{1}{\Delta+\epsilon_{k+q}-\epsilon_k-\hbar\omega_j}-\frac{j_{q0}}{j_{qr}\Delta}\right\}=0 \tag{24}$$

indicating principal part by P.P.

It is the interesting results we have found, on the basis of this equation, that we discuss in the balance of this work—with the aid of tables and graphs of numerical data. But first, we note that it is possible to find the eigenvalues at $q=0$ without any knowledge of the band structure or any numerical analysis. They are

$$\begin{aligned}\hbar\omega_j&=0 \text{ single root}\\&=\Delta \text{ multiple solution (double root at least)}\\&=\Delta\left(1-\frac{j_{0r}}{j_{00}}\right)\text{single root for each distinct } j_{0r}.\end{aligned} \tag{25}$$

The fact that there is a zero eigenvalue at $q=0$ is very encouraging, for the corresponding operator merely rotates the total magnetization partly into the X-Y plane, and the zero eigenvalue expresses the rotationally invariant nature of the approximations made so far. As for the second eigenvalue, all the branches in the continuum must meet at Δ, because at $q=0$ the continuum collapses to a single N-fold degenerate point at Δ. The position of the higher roots depends most of all on the structure of the $J_{0,tt'}$ matrix. In the case when only two d bands are being considered, the ratio $(j_{0r}/j_{00})=-1$. In the case of three d bands, there are two degenerate roots for which $(j_{0r}/j_{00})=-\frac{1}{2}$. In the (unlikely) event that all five d bands are important, then a more complicated eigenvalue spectrum can be expected. Assuming, however, all constant matrix elements then $(j_{0r}/j_{00})=-\frac{1}{4}$, in that case, for $r=1, 2, 3, 4$.

The "acoustic" branches belonging to $r=0$ are independent of the number of d bands. We have calculated these as well as the upper, or "optical" spectra corresponding to the two d band problem. For the numerical calculations, it was necessary to make two principal and related assumptions. These were chosen consistent with electrons, or holes, occupying only a small fraction of the Brillouin zone. First, we systematically neglected umklapp; however, we shall return to this point below. Second, we adopted the effective mass approximation, setting

$$\epsilon_k=\hbar^2k^2/2m^*. \tag{26}$$

We used the convenient units

$$\hbar=2m^*=k_F=\epsilon_{kF}=1, \tag{27}$$

referring F to the "spin-down" Fermi surface.

With these various points in mind, one readily integrates Eq. (24) by means of standard integral formulas and obtains

$$\frac{2}{3}\frac{j_{q0}}{j_{qr}}\left[\frac{1-(1-\Delta)^{3/2}}{\Delta}\right]=\frac{1}{2q}[F(s)-(1-\Delta)F(t)], \tag{28}$$

where

$$F(x)=\frac{1}{x^2}\left[\tfrac{1}{2}(x^2-1)\ln\left|\frac{x+1}{x-1}\right|+x\right] \tag{29}$$

and

$$s=\frac{2q}{\Delta+q^2-\omega_j(q)}\qquad t=\frac{2q(1-\Delta)^{1/2}}{\Delta-q^2-\omega_j(q)}. \tag{30}$$

These transcendental equations were solved for the two-band case on the IBM 7094 by Doherty of this laboratory. The eigenvalues j_{qr} $(r=0,1)$ were assumed to be independent of q for the purposes of this calculation. This was done at first because there was no convenient *a priori* method of deciding on the relative magnitudes of J_{Hu} and J_{Hei}, other than deciding that one or the other vanishes.[8] A more convincing reason appeared after the calculations were performed. The range of q for which the acoustic spin waves lie below the continuum is always less than 0.75 k_F. But, as we shall see, k_F itself must be small compared to $\frac{1}{2}\pi/a$ in order that the neglect of umklapp be valid, and that ferromagnetism be stable versus antiferromagnetism. We shall return to this point subsequently. When these arguments are applied to Eq. (20), it is seen that at the very worst if J_{Hu} were somehow unexpectedly to vanish, the assumption of a constant eigenvalue would lead to not more than 20% error in the results. But with more realistic assumptions about k_F and the relative magnitudes of the two exchange forces, the maximum error might be as little as 1%.

In Table I and Figs. 1–5, we present the results of the spin-wave calculations for several values of Δ. Note that there is a universal spectrum for $\Delta\geq 1$, when $\hbar\omega_j$ is expressed in units of Δ. Note also that there is a maximum wavevector for solutions *even* in the continuum.

[8] Hund's rule coupling is of the order of *several* eV in the transition atoms, and, therefore even when screened in the metal is quite substantial enough to account for magnetic energies $kT_c\sim 0.1$ eV. On the other hand, the magnitude and even *the sign* of Heisenberg nearest neighbor exchange in the metals has been the object of dispute rather than agreement. The Heitler-London scheme, in which it has been often calculated, is in current disrepute [C. Herring, Rev. Mod. Phys. **34**, 631 (1962)]. Probably, the nearest-neighbor exchange energy is in the range $0-\frac{1}{2}$ eV in magnitude, at most.

TABLE I. Spin-wave energies $\hbar\omega$ for the acoustic branch below continuum (ac.) and the optical branch above continuum (opt.), at various values of q (not evenly spaced), for $\Delta=0.3$, 0.5, and $\Delta\geq 1.0$. Small—q behavior of acoustic branch is given by Eqs. (31)–(33) of text. Cutoff momentum can be found by: $s(q)=+1$ (ac.) and $s(q)=-1$ (opt.), and is defined as the point where the spin-wave spectrum joins the continuum. The function $s(q)$ is given in Eq. (30) of the text. The unit of energy is $\epsilon_{F\downarrow}$ (the Fermi energy measured relative to the bottom of the band) and the unit wave vector is $k_{F\downarrow}$, the corresponding Fermi wave vector, as given in Eqs. (26) and (27).

$\Delta=0.3$, q $(k_{F\downarrow})$	0.05	0.06	0.07	0.08	0.09	0.10	0.11	0.12	0.13	0.14	0.15
$\hbar\omega_{ac.}$ $(10^{-4}\epsilon_{F\downarrow})$	0.72	1.01	1.35	1.73	2.13	2.54	2.94	3.32	3.65	3.86	3.86
$\hbar\omega_{opt.}$ $(\epsilon_{F\downarrow})$	0.618	0.626	0.635	0.645	0.656	0.668	0.680	0.694	0.708	0.723	0.738
$\Delta=0.5$, q $(k_{F\downarrow})$	0.05	0.08	0.11	0.14	0.17	0.20	0.22	0.23	0.26	0.27	0.29
$\hbar\omega_{ac.}$ $(10^{-3}\epsilon_{F\downarrow})$	0.138	0.351	0.648	1.013	1.423	1.841	2.094	2.203	2.379	2.340	1.657
$\hbar\omega_{opt.}$ $(\epsilon_{F\downarrow})$	1.01	1.03	1.05	1.08	1.11	1.15	1.17	1.19	1.24	1.25	1.29
$\Delta\geq 1.0$, q $(k_{F\downarrow})$	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.50	0.60	0.70	0.75
$\Delta^{-1}\hbar\omega_{ac.}$ (10^{-2})	0.199	0.445	0.785	1.213	1.722	2.303	2.943	4.332	5.681	6.532	6.250
$\Delta^{-1}\hbar\omega_{opt.}$	2.02	2.04	2.07	2.11	2.16	2.22	2.29	2.45	2.66	2.91	3.06

We see that there is one point on which the present results agree with conventional spin-wave theory for the Heisenberg Hamiltonian. Due to the initial parabolic behavior of the lowest acoustic branch, the magnetic specific heat, and the deviations from saturation magnetization must obey Bloch's $T^{3/2}$ law at low temperature. [The prediction of the original band theories of a T^2 law near $T=0$, or worse, of a law $\exp(-\Delta/kT)$, is not confirmed, and we suppose the discrepancy caused by neglect of the collective spin-wave modes in the earlier theories.] On the other hand, as we have already mentioned, the long-wavelength acoustic branch results were later correctly explained (by Herring and Kittel[4] and others[6]) on the basis of very general considerations. We supplement these with the following details.

Let us write the increasing portion of the acoustic spectrum in the form,

$$\omega(q)=\frac{q^2}{\mu(q)}=\frac{q^2}{\mu(0)}+O(q^4). \tag{31}$$

Then $\mu(0)$ is the "effective mass" of a spin wave, in units of the electronic mass m^*. By an expanssion of the exact Eqs. (28)–(30), one can derive the formula,

$$\mu(0)=\frac{1-(1-\Delta)^{3/2}}{1+(1-\Delta)^{3/2}-\frac{4}{5}[(1-(1-\Delta)^{5/2})/\Delta]}m^*, \qquad \Delta\leq 1 \tag{32}$$

and

$$\mu(0)=(5/\Delta)m^*, \quad \Delta\geq 1. \tag{33}$$

In Figs. 2 and 3 we demonstrate graphically the limits of validity of the parabolic approximation. Throughout much of the range, the acoustic spectrum would appear to be well-approximated by a parabola *plus* quartic corrections, such as $1/5q^2-1/10q^4$ in the case of $\Delta\geq 1$. But our neglect of any possible q dependence of j_{q0}, m^*,

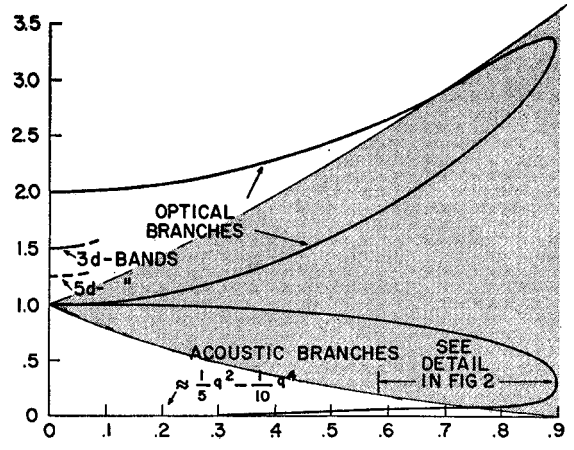


FIG. 1. Solutions of Eq. (28) in the case of two active d bands, coupling constant $\Delta\geq 1.0$. The vertical axis measures $\hbar\omega/\Delta$, and the horizontal axis the wave vector q in units of $k_{F\downarrow}$. The shaded area indicates the continuum of scattering solutions of Eq. (22). Approximate formula for lowest portion of acoustic branch is given as $(\frac{1}{5}q^2-\frac{1}{10}q^4)$, for purposes of low-temperature expansions. This branch below the continuum, and the optical branch above the continuum correspond to bound-state spin waves of infinite lifetime (within RPA). In the case of three d bands and five d bands, only the optical spectra are changed, as indicated.

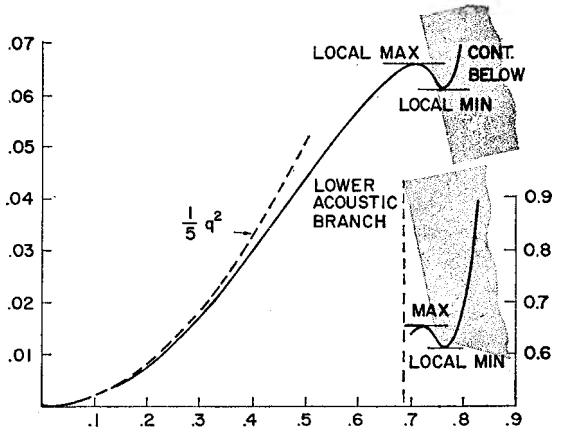


FIG. 2. Lower acoustic branch of Fig. 1 on a vertical scale expanded 50 times. Approximate fit of asymptotic formula $\lim(\hbar\omega/\Delta)=\frac{1}{5}q^2$ as $q\to 0$ for $\Delta\geq 1$, is shown, and details of bound-state crossing into continuum.

and umklapp would have its first effect on the *quartic* terms. Moreover, as they are very tedious to calculate explicitly, we do not carry out the analytic expansion beyond the effective mass approximation given above.

FERROMAGNETISM OR ANTIFERROMAGNETISM?

For $\Delta \geq 1$, all electrons have spin down. This is an eigenstate of the Hamiltonian of Eq. (11) as well as of the kinetic energy and exchange interactions *separately*. According to the criterion of "spin-wave stability" this is, moreover, the true ground state,[9] since all the spin-wave energies we have calculated are positive. However, let us examine this more closely.

Recently, in attempting to explain the antiferromagnetism of chromium by the band theory, Tachiki and Nagamiya[10] found that when the Fermi sphere

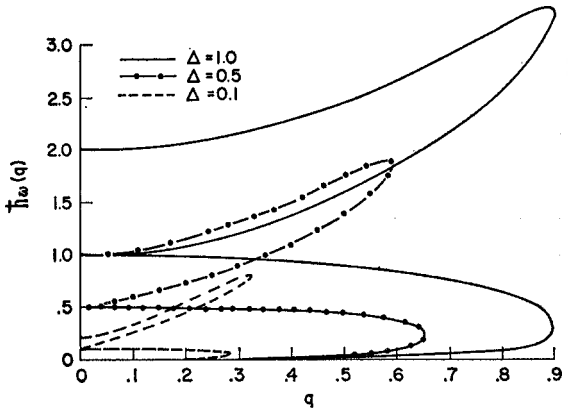


FIG. 4. Spectra for $\Delta = 1.0, 0.5, 0.1$, plotted on same scale for comparison.

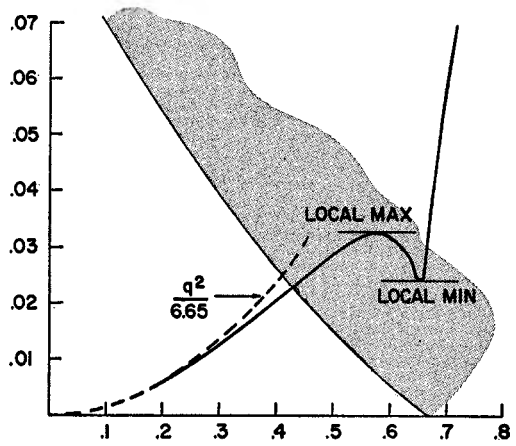


FIG. 3. Same as Fig. 2, but $\Delta = 0.9$ for comparison.

more or less half-filled the Brillouin zone, and when the coupling was strong enough to produce localized magnetic moments (i.e., when criterion (17) is obeyed), that these would be antiferromagnetically ordered rather than parallel as in ferromagnetism.[11,12] This may be seen in the present theory also. If the Fermi surface was neither small nor spherical, and umklapp became important, then the calculated spin-wave spectrum obtained from Eq. (24) might well become negative and achieve its minimum value for some $q_0 \neq 0$. The ground state would then be, to some approximation, a spiral antiferromagnetic structure of spiral pitch q_0. That is, once the coupling constant became strong enough to produce some sort of magnetism, *which* magnetic structure might be stablest would depend on the particular Fermi surface and crystal structure.[11,13] This is quite analogous to what we once discovered in connection with the indirect exchange theory[13]: ferromagnetism for small k_F, antiferromagnetic spiral configurations for large k_F. In the present case, with the hole-electron symmetry, if the bands are almost empty or almost full, there can occur ferromagnetism, and in half-filled bands, most likely antiferromagnetism, with umklapp playing a major role (and consequently, the dependence on crystal structure).

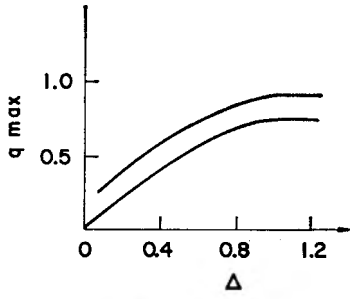


FIG. 5. Cutoff wave vector q_{max} as function of coupling constant Δ. Upper curve is maximum wave vector at which solutions of Eq. (28) exist. The lower curve is wave vector at which acoustic branch enters the continuum, and at approximately the same value the optical branch also crosses into the continuum.

[9] "Spin-wave stability" is a necessary, but *not sufficient*, criterion for ferromagnetism. Cf. D. Mattis, Phys. Rev. **130**, 76 (1963).

[10] M. Tachiki and T. Nagamiya, Phys. Letters **3**, 214 (1963). The very interesting related problem of spin waves in a band-theoretic antiferromagnetic remains to be studied.

[11] It would be confusing if the definition of "ferromagnetism" was "same magnetic structure as iron," because when iron is in its γ phase (face-centered cubic) the magnetic moments are *antiferromagnetically* disposed (see Ref. 12). The problems this poses in semantics are enormous, but the agreement between theory (Ref. 10, 13) and experiment (Ref. 12) is pleasing.

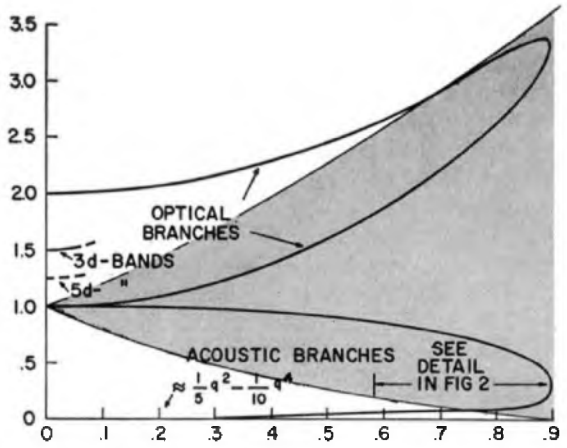
[12] S. C. Abrahams, L. Guttman, and J. S. Kasper, Phys. Rev. **127**, 2052 (1962). Assuming that iron, with 2.2 μ_B/atom, has a half-filled B.Z., the antiferromagnetism is not surprising. Conversely, all crystallographic phases of pure nickel (0.6 μ_B/atom) should remain ferromagnetic, as k_F is sufficiently small that umklapp may be neglected. But a chemical shift downward of the Fermi level in Ni might cause that substance to become antiferromagnetic also.

[13] D. Mattis and W. Donath, Phys. Rev. **128**, 1618 (1962).

In any event, the effective mass approximation used in the present calculations is most accurate when there is a small number of electrons (or holes), and in that case also, umklapp is of no consequence. But, as these are assumptions compatible with the existence of ferromagnetism, according to the previous arguments, they are therefore quite proper in calculating the properties of a ferromagnet (but not of an antiferromagnet), and are self-consistent.

ACKNOWLEDGMENTS

We would like to thank Dr. C. Herring for a very interesting discussion on the subject of magnetism in metals, and Professor T. Nagamiya for discussing his model of antiferromagnetism. We are most grateful to W. Doherty for high-accuracy numerical computations of the solutions to Eq. (28), and to Dr. T. Schultz for many interesting comments on the instability of collective modes in the continuum.



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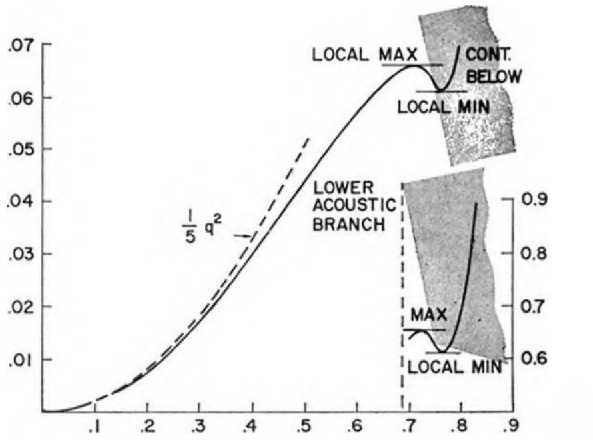

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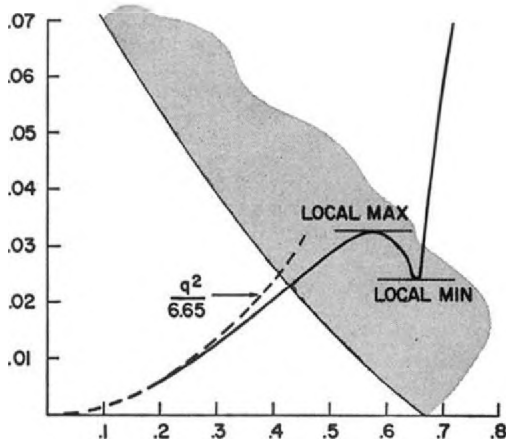

FIG. 3. Same as Fig. 2, but $\Delta = 0.9$ for comparison.